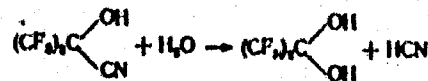


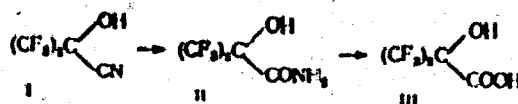
Brief Communications. Fluorinated Ketones.
Bis-(trifluoromethyl)-glycolic Acid

77292

SOV/63-4-6-26/37



(I) by moderate heating is hydrolyzed to amide of bis-(trifluoromethyl)-glycolic acid (II) and, under drastic conditions, bis-(trifluoromethyl)-glycolic acid (III) is formed.



Card 2/4

The obtained compounds, starting materials, yields, and properties are given in the table below:

Brief Communications. Fluorinated Ketones.
Bis-(trifluoromethyl)-glycolic Acid

77292
SOV/63-4-6-26/37

Nr	Compound	Starting Materials
I	$(CF_3)_2C(OH)CN$	Hexafluoroacetone + HCN + piperidine
II	$(CF_3)_2C(OH)CONH_2$	I + H_2SO_4
III	$(CF_3)_2C(OH)COOH$	I + H_2SO_4
IV	$(CF_3)_2C(OH)COOC_2H_5$	III + $(C_2H_5)_2O$ + H_2SO_4
V	$(CF_3)_2C \begin{matrix} \swarrow O-C(CF_3)_2 \\ \searrow COO \end{matrix}$	I + hexafluoroacetone hydrate + H_2SO_4
VI	Anilide of bis- (trifluoromethyl)- glycolic acid	-
VII	$(CF_3)_2C \begin{matrix} \swarrow OH \\ \searrow OH \end{matrix} 2C_6H_5NH_2$	V + $C_6H_5NH_2$

Card 3/4

Brief Communications. Fluorinated Ketones
Bis-(trifluoromethyl)-glycolic Acid

77292
SOV/63-4-6-26/37

Yield (%)	mp	bp	d_4^{20}	n_D^{20}
61.2	-	107.5	1.5585	1.298
29.6	71-73	-	-	-
62.2	78-82	153-155	-	-
90.6	-	120	1.424	1.3270
15.0	-	84-85	1.7189	1.2885
80.2	101-102	-	-	-
29.7	64-65	-	-	-

There is 1 table; and 11 references, 4 Soviet, 3 German, 1 Dutch, 1 French, 2 U.K. The U.K. references are: R. A. Darrall, F. Smith, M. Stacey, J. C. Tatlow, J. Chem. Soc., 1951, 2329; M. W. Buxton, M. Stacey, J. C. Tatlow, *ibid*, 1954, 366.

ASSOCIATION: Institute of Element-Organic Compounds, Academy of Sciences, USSR (Institut elementoorganicheskikh soedineniy Akademii nauk SSSR)

SUBMITTED: July 18, 1959

Card 4/4

5.3700

77299
SOV/63-4-6-33/37

AUTHORS: Sterlin, R. N., Pinkina, L. N., Knunyants, I. L.,
Nezgovorov, L. P.

TITLE: Radical Exchange of Perfluoroalkenylmagnesium Derivatives

PERIODICAL: Khimicheskaya nauka i promyshlennost', 1959, Vol 4, Nr 6,
pp 809-810 (USSR)

ABSTRACT: Radical exchange was studied in the system perfluoro-
vinyl iodide-phenylmagnesium bromide, in absolute
ether. To show exchange, arsenic trichloride or carbon
dioxide was added to the system. In the first case
tri-(trifluorovinyl)-arsine (11.3% yield, based on per-
fluorovinyl iodide), and in the second case perfluoro-
acrylic acid (32% yield, based on perfluorovinyl
iodide) were obtained. This shows that in systems $RMgX$
 $+ R'X \rightarrow R'MgX + RX$ radical exchange takes place only
when there exists a sufficient difference between the
electrophilicities of R and R'. There are 6 references,
2 Soviet, 4 U.S. The U.S. references are: O. R. Pierce,

Card 1/2

Radical Exchange of Perfluoroalkenyl-
magnesium Derivatives

77299

SOV/63-4-6-33/37

A. F. Meiners, E. T. McBee, J. Am. Chem. Soc., 75,
2516 (1953); H. Gilman, H. L. Jones, *ibid.*, 51, 2840
(1929); P. Tarrant, D. A. Warner, *ibid.*, 76, 1624 (1954);
Rochow, The chemistry of Organometallic Compounds (1957).

SUBMITTED: August 1, 1959

Card 2/2

5.3700

77300

SOV/63-4-6-34/37

AUTHORS:

Sterlin, R. N., Yatsenko, R. D., Pinkina, L. N., Knunyants, I. L.

TITLE:

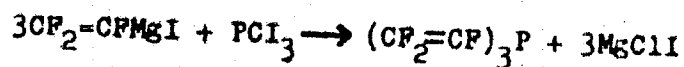
Perfluorovinylhalophosphines

PERIODICAL:

Khimicheskaya nauka i promyshlennost', 1959, Vol 4, Nr 6, pp 810-811 (USSR)

ABSTRACT:

On the basis of the previously investigated (Izv. AN SSSR, 1959, Nr 8) reaction of perfluorovinylmagnesium iodide with SiCl_4 , the authors obtained similarly new tri-(trifluorovinyl)-phosphine (yield 35.4%; bp 99-101° C; $n_D^{23.5}$ 1.3909) in the reaction:



It was also shown that amides of the type $\text{CIP}(\text{NR}_2)_2$ react easily with R'MgX (where R' is an alkyl or ϕ -alkenyl) and form substituted amides of alkyl- or

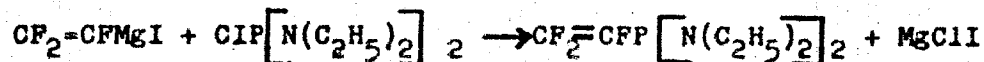
Card 1/4

Perfluorovinylhalophosphines

77300

SOV/63-4-6.34/37

or ϕ -alkenylphosphinous acid. For example, tetra-
ethyldiamide of perfluorovinylphosphinous acid bp
89-90° C at 11 mm; n_D^{20} 1.4470) was obtained in 53.6%
yield in the reaction:



Similarly, diethylamide of di-(trifluorovinyl)-phos-
phinous acid (bp 60° C at 25 mm; n_D^{20} 1.4098) was obtained
in 37.5% yield on redistillation of fraction 49-53° C
received in the reaction:



The fractional distillation must not be carried to com-
pletion as the residue decomposes explosively. It was
shown further that amides of the type $R'P(NR_2)_2$ are

Card 2/4

decomposed by dry HCl and form primary and secondary

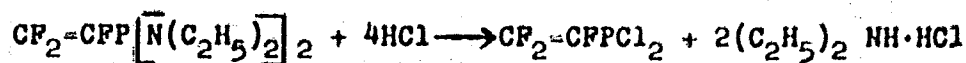
Perfluorovinylhalophosphines

77300

SOV/63-4-6-34/37

chlorophosphines. Decomposition of perfluorovinylphosphinous tetraethyldiamide with dry HCl gave perfluorovinylidichlorophosphine (yield 66%; bp 81.5-82° C;

n_D^{19} 1.4412);



Similarly, the decomposition of di-(trifluorovinyl)phosphinous diethylamide gave di-(trifluorovinyl)chlorophosphine (yield 60%; bp 94-95° C; n_D^{28} 1.4095;

$(CF_2=CF)_2PCl$). Also ethyldichlorophosphine ($C_2H_5PCl_2$)

was synthesized. The first two chlorophosphines in reaction with antimonous fluoride were transformed into the corresponding perfluorovinylfluorophosphines, colorless liquids easily flaring up in air. Perfluorovinylidichlorophosphine thus gave perfluorovinylidifluorophosphine (yield 64%; bp 2-3° C):

Card 3/4

Perfluorovinylhalophosphines

77300

SOV/63-4-6-34/37



Similarly, di-(trifluorovinyl)-chlorophosphine gave di-(trifluorovinyl)-fluorophosphine ($\text{CF}_2=\text{CF}$)₂PF (yield 50%; bp 63-65° C). There are 3 references, 1 U.K.; 1 German, 1 Soviet. The U.K. reference is: F. Bennett, H. Emeleus, R. Haszeldine, J. Chem. Soc., 1953, p 1565.

SUBMITTED: June 1, 1959

Card 4/4

5 (3)

AUTHORS:

Sterlin, R. N., Kunyants, L. L.,
Pinkina, L. N., Yatsenko, R. D.

SOV/62-59-8-29/42

TITLE:

Tetrafluorovinylsilane

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
1959, Nr 8, pp 1492-1493 (USSR)

ABSTRACT:

Starting from a consideration of the reaction of tetrachlorosilicon with alkyl- and aryl silanes and other organic silicon (or magnesia) halogenides, the present paper describes the attempted gradual substitution for the Cl-atom in SiCl_4 of a perfluorovinyl group. As expected, the introduction of such a group caused a decrease in the electron density in the central Si-atom. Thus the substitution of further groups is progressively facilitated. The tetrafluorovinylsilane is stable in aqueous acid solutions; in bases it is quantitatively split into trifluoroethylene which has been identified by its dibromide. The reaction is described in the experimental part. There is 1 reference.

SUBMITTED:

February 11, 1959

Card 1/1

5 (3)

AUTHORS:

Sterlin, B. N., Li-Wei-Kang,
Kunyants, I. L.

SOV/62-59-8-37/42

TITLE:

Perfluorodiviny Mercury

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
1959, Nr 8, p 1506 (USSR)

ABSTRACT:

It is reported that perfluorodiviny mercury (C_4F_6Hg) was obtained from perfluorovinyl magnesium iodide and mercury chloride in an ether solution at $-10-5^\circ$ as a colorless liquid with a disagreeable odor (slightly soluble in water). C_4F_6Hg reacts rather easily with iodine while perfluorovinyl iodide is formed. The physical properties of C_4F_6Hg differ considerably from those of the perfluoroalkyl mercury derivatives. These have a high melting point and are easily soluble in water. In comparison to the compounds investigated they are considered to be halogene derivatives of Hg whereas the former are designated vinyl derivatives of mercury in which the pseudohalogenous character of the perfluorovinyl radical is not prominent. There is 1 reference.

Card 1/2

5(3)

AUTHORS:

Dmitriyev, M. A., Sokol'skiy, G. A., Knunyants, I. L.,
Academician

SOV/20-124-3-24/67

TITLE:

The Affiliation of Sulfur Trioxide on Fluorolefins
(Prisoyedineniye sernogo angidrida k ftorolefinam)

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 124, Nr 3, pp 581-582
(USSR)

ABSTRACT:

A description is given of the adducts of sulfur trioxide to tetrafluoroethylene, trifluorochloroethylene, trifluoroethylene and hexafluoropropylene. According to the individual modifications of the sulfur trioxide employed, β -sultones (with α -SO₂) or β -pyro-sultones (with dimeric SO₂) are formed. The adducts react energetically with various organic and inorganic substances. In the majority of cases, derivatives of fluorine-containing α -sulfofluoride-carboxylic acids are formed in this process. - From the reaction of sulfofluoride-difluoroacetic chloride with antimony trifluoride a preparation is obtained which is identical with the initial tetrafluoroethane- β -sultone. From this transformation cycle, from several other properties, as well as from the infrared spectra

Card 1/2

The Affiliation of Sulfur Trioxide on Fluorolefins

SOV/20-124-3-24/67

of the adducts and the derivatives of the α -sulfofluoride-carboxylic acids it can be concluded that, on the affiliation of SO_3 to the fluorolefins, a dynamic mixture of two isomers is formed; a cyclic β -sultone and a linear difluoride of sulfo-carboxylic acid. The physical data of the preparations thus obtained are given in tables. There are 2 tables.

SUBMITTED: October 16, 1958

Card 2/2

5(3)

AUTHORS:

Knunyants, I. L., Academician,
Dyatkin, B. L., German, L. S.

SOV/20-124-5-28/62

TITLE:

Reactions of Hexafluoro Butadiene-1,3 With Alcohols and Amines
(Reaktsii geksafторbutadiyena-1,3 so spirtami i aminami)

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 124, Nr 5, pp 1065-1068
(USSR)

ABSTRACT:

The reactivity of the 1,3-dienes of the perfluoro-carbon series has hardly been investigated (Refs 1-3). The reactions with nucleophilic reagents which very characteristic of fluoro olefins, have hitherto not been investigated in the case of perfluoro butadiene. These reactions are of particular interest for an understanding of the nature of the conjugated bonds in perfluorated dienes. Here, as distinguished from diene hydrocarbons, a negative rather than a positive charge is to be transmitted along the chain. By the interaction of perfluoro butadiene with sodium ethylate in ethanol the authors obtained a substance which separated HF and formed 1,4-diethoxyperfluoro butadiene-1,3 when isolation in a pure condition was attempted. The treatment of the latter compound with concentrated sulphuric acid resulted in the formation of the diethyl esters of

Card 1/3

Reactions of Hexafluoro Butadiene-1,3 With Alcohols
and Amines

SOV/20-124-5-28/62

fluoro ethylene-1,2-dicarboxylic acid. This ester was transformed into 3-carbethoxy-pyrazolone-5 by the action of hydrazine hydrate. Thus, perfluorobutadiene reacts with two alcohol molecules in the presence of alcoholate. In this connection the terminal carbon atoms are subjected to the nucleophilic attack. Heating of perfluoro butadiene with alcohol in the presence of triethylamine causes the addition of one alcohol molecule. The infrared spectrum and the nuclear-magnetic resonance of F^{19} suggest a 1,4 affiliation. Under mild conditions perfluoro butadiene reacts with the secondary and primary aliphatic amines. With diethylamine it forms the unstable 1-diethylamine-perfluorobutadiene-1,3, which is readily hydrolyzed to form the diethylamide of α -hydroperfluoro vinylacetic acid. A similar reaction is that of perfluoro butadiene with piperidine. By the interaction of perfluoro butadiene with ethylamine and the hydrolysis of the reaction products ethylamide of the last mentioned acid and bis-ethylamide of fluoro ethylene-1,2-dicarboxylic acid was produced. In this case the resulting bis-ethylamide of symmetrical

Card 2/3

Reactions of Hexafluoro Butadiene-1,3 With Alcohols
and Amines

SOV/20-124-5-28/62

difluorosuccinic acid loses only a single HF molecule (as in the case of the ester) and forms a corresponding derivative of fluoro ethylene-1,2-dicarboxylic acid. There are 3 references.

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR
(Institute for Elemental-Organic Compounds of the Academy of Sciences, USSR)

SUBMITTED: November 21, 1958

Card 3/3

5 (3)

AUTHORS:

Kmamyants, I. ~~Academician,~~
Bykhovskaya, M. G., Prosin, V. N.

SOV/20-127-2-28/70

TITLE:

Interaction Between η -Olefines and Hydroxylamine

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 2, pp 337-340 (USSR)

ABSTRACT:

The addition of hydroxylamine, a nucleophilic reagent, to perfluoro olefines has a long time not been investigated. Hydroxylamine is easily added to η -propylene and η -isobutylene, as it is expected. The initially produced addition products are unstable and separate spontaneously HF during the reaction course. They are in this case transformed into fluorides of the hydroxamic acids of corresponding 2-mono-hydro-perfluoro carboxylic acids. The escaping HF is bound by hydroxylamine (see Scheme). The produced fluorides of the 2-hydro-perfluoro-propio-hydroxamic acid and 2-hydro-perfluoro-isobutyro-hydroxamic acid were isolated as complexes with alcohol or ether (according to the solvent used). They are colorless transparent liquids with an acrid smell insoluble in water, well soluble in usual organic solvents. Boiled with an aqueous bicarbonate solution, they react with ferric chloride positively to hydroxamic acid. Their structure see scheme (III) and (IV). The hydrolysis products of

Card 1/2

Interaction Between α -Olefines and Hydroxylamine

SOV/20-127-2-26/70

the anhydride of fluoric acid of the first of the produced acids with water, hydrochloric- and sulphuric acid are described. The methyl ester of the 2-hydro-perfluoro-propionic acid and sodium fluoride were isolated as a result of the reaction between the ether complex of the same acid and the alcoholic solution of sodium methylate. This confirms the existence of fluorine as acid fluoride in this compound. The obtained hydroxamic acids can be easily distilled in vacuum. They cleave off 2 HCl molecules in the case of heating with thionyl chloride and form cyclic compounds (see Scheme). The latter cleaves off sulphur gas under the influence of alkali and produces a hydroxamic acid salt. There is 1 Soviet reference.

SUBMITTED:

May 12, 1959

Card 2/2

5(3)

AUTHORS:

Lin'kova, M. G., Patrina, N. D.,
Knunyants, I. L., Academician

SOV/20-127-3-23/71

TITLE:

A New Method of Producing Propiothiolactone.

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 3, pp 564-566
(USSR)

ABSTRACT:

Under the influence of chloroacetic acid ester, β -propiothiolactone is developed by β -mercapturic acids (Refs 1-3) in the presence of triethylamine. It proved, however, that the same thiolactones can be developed more easily by an influence of H_2S on the chlorides of β -halogen-carboxylic acids. The extension of the reaction (I) on the chlorides of other β -halogen-carboxylic acids showed that the new method is of universal validity for the production of β -propiothiolactone. A careful investigation of the formation conditions of α -propiothiolactone showed that, according to the permanence of the developing β -propiothiolactone, in some cases sodium sulphide may be used instead of H_2S . In order to prevent a splitting of the developing thiolactone, the temperature

Card 1/2

5 (3)

AUTHORS:

Lin'kova, M. G., Patrina, N. D.,
Knunyants, I. L., Academician

SOV/20-127-4-19/60

TITLE:

Addition of Alkyl-sulphenchlorides to Acrylic Acid Derivatives

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 4, pp 799-802
(USSR)

ABSTRACT :

According to the polarity of the chlorides, referred to in the title the addition mentioned there does not present any difficulties resulting in the formation of α -alkyl-thio- β -chlorine-substituted acids (see Scheme) (Ref 1). It was necessary to check the data contained in reference 2, in which the author ascribes the structure of the α -chloro- β -alkyl thioderivatives of propionic acid to these addition products (see Scheme). Further investigations of the reaction mentioned in the title, by the authors have again confirmed the opinions stated by them before and have refuted the opinion expressed in reference 2, i. e. the addition of the ethyl-sulphen-chloride to acrylic, methacrylic, and dimethyl-acrylic acid, to the acrylonitrile, as well as to the acid chloride and the ethyl ester of dimethyl acrylic acid results in the formation of β -chloro- α -alkyl thioderivatives of propionic acid (see Scheme). During this

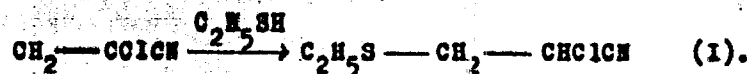
Card 1/3

Addition of Alkyl-sulphenchlorides to Acrylic Acid
Derivatives

SOV/20-127-4-19/60

reaction the ethyl-sulphen chloride is easily added to esters, while it is more difficult to add it to acids and nitriles, and most difficult to add it to acid chlorides (Ref 1). From the acid chlorides of β -chloro- α -alk thioderivatives of propionic acid corresponding β -propiothiolactones (Ref 5) were obtained by means of H_2S (see Scheme). With an order other than that illustrated by the scheme, the formation of the said lactones would be impossible. Without cogent reasons Gundermann has given his consent to the assertions of Brintsinger (Ref 2) according to which the alkyl thiogroup assumes a β -position under the action of sulphen chlorides on acryl systems, whereas the chlorine atom assumes an α -position. To give a definite explanation of this problem the authors prepared α -chloro-ethyl thiopropionitrile (I) and α -ethyl thio- β -chloro propionitrile (II) and compared their properties with one another. By adding ethyl mercaptan to α -chloro acrylonitrile (Ref 7) the following reaction was brought about:

Card 2/3



STERLIN, R.M. [translator]; KUNYANTS, I.L., akademik, red.;
VITKOVSKIY, D.P., red.; RABINOVICH, F.V., red.; ZASHCH'SKAYA,
V.F., tekhn.red.

[Modern experimental methods in organic chemistry] Sovremennye
metody eksperimenta v organicheskoi khimii. Pod red. I.L.
Kuniantse. Moskva, Gos.nauchno-tekhn.isd-vo khim.lit-ry, 1960.
627 p. (MIRA 14:1)

(Chemistry, Organic--Experiments)

VATSULIK, Pavel [Vaculik, Pavel], inzh.dr.; ARTEM'YEV, A.A., kand.tekhn.
nauk [translator]; VOL'YKON, B.M. [translator]; KHUNYANTS, I.L.,
akademik, red.; ZAKHAR'YEVSKIY, V.A., red.; PRIDANIYEVA, S.V.,
tekhn.red.

[Chemistry of monomers] Khimii monomerov. Pod red. I.L.
Khuniantse. Moskva, Izd-vo inostr.lit-ry. Vol.1. 1960. 738 p.
(MIRA 14:3)

(Polymers)

(Chemistry, Organic)

KNUNYANTS, I.L.; GOLUBEVA, N.E.; KIL'DISHEVA, O.V. (Moskva)

Principles underlying the production of specific carcinolytic
preparations. Usp. soov. biol. no.2:167-173 8-0 '60,

(MIRA 13:11)

(CYTOTOXIC DRUGS)

Knunyants, I. L.

82010
8/062/60/000/02/03/012
B003/B066

5.3600

AUTHORS:

Knunyants, I. L., German, L. S., Dyatkin, B. L.

TITLE:

Reactions of Fluoro-olefins. 11th Report. Interaction of Compounds of the Perfluoro Isobutylene Series With Amines and Ammonia

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 2, pp. 221 - 230

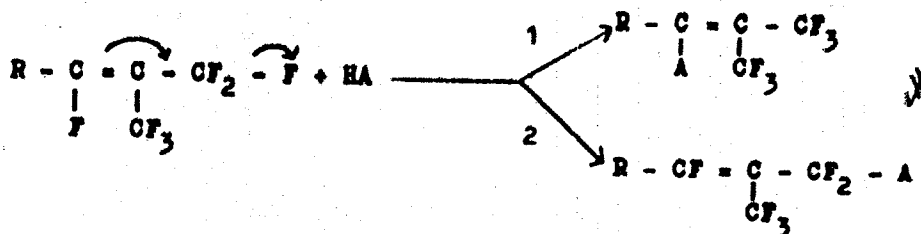
TEXT: The authors investigated the reactions of 1-alkyl-, 1-alkoxy-, and 1-aryl-perfluoro isobutylenes with amines and ammonia. (The following compounds were subjected to the experiments: 1-phenyl perfluoro isobutylene, 1-phenyl perfluoro propylene, $\alpha, \beta, \beta, \beta$ -tetrafluoro propiophenone, 1-phenyl-1,2-dibromo-perfluoro propane, 1-butyl perfluoro isobutylene, 1-styryl-perfluoro isobutylene, 1-ethylperfluoroisobutylene, 1-isoamylperfluoroisobutylene, anhydrous ammonia, ammonium hydroxide, ethyl amine, diethyl amine, and piperidine. The preparation of the compounds and their reactions are described in detail in the experimental part of the paper.) 1-alkyl- and 1-aryl perfluoro isobutylenes react with

Card 1/3

Reactions of Fluoro-olefins. 11th Report.
Interaction of Compounds of the Perfluoro
Isobutylene Series With Amines and Ammonia

82040
S/062/60/000/02/03/012
B003/B066

nucleophilic agents in two ways according to the following scheme:



Whether this reaction proceeds according to 1 or 2, depends on the character of the olefin as well as on the attacking reagent. Under the action of anhydrous NH_3 the reaction takes place in all perfluoro isobutylenes investigated. 1-alkyl- and 1-aryl perfluoro isobutylenes react with secondary amines according to Scheme 2. The action of excess NH_4OH eliminates fluorine completely. There are 5 references: 2 Soviet, 1 German, 1 American, and 1 Canadian.

Card 2/3

Reactions of Fluoro-olefins. 11th Report.
Interaction of Compounds of the Perfluoro
Isobutylene Series With Amines and Ammonia

CIA-RDP86-00513R000723330002-1
82040
S/062/60/000/02/03/012
B003/B066

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk
SSSR (Institute of Elemental-organic Compounds of the
Academy of Sciences USSR)

SUBMITTED: July 4, 1958

Card 3/3

KUNYANTS, I. L.

82011
8/062/60/000/02/04/012
B003/B066

5.3600

AUTHORS:

Kunyan, I. L., Dyatkin, B. L., German, L. S.,
Mochalina, Ye. P.

TITLE:

Reactions of Fluoro-olefins. 12th Report. Interactions of
Polyfluoro-chloro Butenes With Alcohols

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk.
1960, No. 2, pp. 231 - 236

TEXT: The authors investigate the action of sodium methylate and ethylate on linear dimers of 1,2-difluoro-1,2-dichloro ethylene and trifluoro-chloro ethylene. The experiment is described in detail in the experimental part of the paper. The structure was clarified by means of infrared spectrography. The investigations revealed that the reaction of 1,2,3,4-tetrafluoro-1,3,4,4-tetrachloro butene-1 with the alcoholates mentioned yields 1,1,1-trialkoxo-2,3,4-trifluoro-4,4-dichloro butene-2. When treating the linear dimer of trifluoro-chloro ethylene with the alcoholates, 3-alkoxy-4-chloro-perfluoro butene-1 results. The linear dimer of trifluoro-chloro ethylene was identified to be a mixture of

Card 1/2

Reactions of Fluoro-olefins. 12th Report.
Interactions of Polyfluoro-chloro Butenes
With Alcohols

820.1
S/062/60/000/02/04/012
B003/B066

3,4-dichloro-perfluoro butene-1 and 1,4-dichloro-perfluoro butene-2
(with the latter being predominant). There are 17 references: 4 Soviet,
10 American, 1 Belgian, and 1 German.

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk
SSSR (Institute of Elemental-organic Compounds of the
Academy of Sciences USSR)

SUBMITTED: July 4, 1958 (initially)
July 31, 1959 (after revision)

Card 2/2

SOKOL'SKIY, G.A.; KHMUTANTS, I.L.

Preparation of nitrosyl fluoride and some of its properties.

Izv.AN SSSR.Otd.khim.nauk no.5:779-783 My '60.
(MIRA 13:6)

(Nitrosyl fluoride)

DMITRIYEV, M.A. [deceased]; SOKOL'SKIY, G.A.; KEHNTANTS, I.L.

Fluorine-containing β -sulfones. Report No.1: Addition of
sulfuric anhydride to fluorolefins. Izv.AN SSSR Otd.khim.
nauk no.5:847-851 May '60. (MIRA 13:6)
(Sulfones)

DMITRIYEV, M.A.; SOKOL'SKIY, G.A.; KRUYANTS, I.I.

Fluorine-containing β -sulfones. Report No.2: Hydrolysis of
tetrafluoroethane- β -sulfone. Izv.AN SSSR.Otd.khim.nauk
no.6:1035-1038 J1 '60. (MIRA 13:7)
(Sulfones) (Fluorine organic compounds)

82692

3/062/60/000/008/006/012
B004/B054

5.360

AUTHORS:

Knunyants, I. L., Krasuskaya, M. P., and Mysov, Ye. I.

TITLE:

Reactions of Fluoro Olefins. 13. Catalytic Hydrogenation
of Perfluoro Olefins 1

PERIODICAL:

Investiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk,
1960, No. 8, pp 1412-1418

TEXT: In previous papers (Refs. 3, 4) the authors had been dealing with the hydrogenation of fluoro olefins, which easily proceeds on a palladium- or nickel catalyst. In the present paper they report on the hydrogenation of tetrafluoro- and trifluoro ethylene as well as on the fact that the products of hydrogenation of some hydrocarbon fluorides easily split off hydrogen fluoride under the action of alkali; here, fluoro olefins are formed which cannot, or can only with great difficulty, be produced by means of the usual methods of halogenation. In this connection, the authors give the following reaction chains: Perfluoro isobutylene is hydrogenated to 1,1,3,3,3-pentafluoro-2-trifluoromethyl propane (I), which in aqueous alkali solution easily yields HF, and forms 1,3,3,3-tetrafluoro-2-trifluoromethylpropene-1 (II) the structure of which was established by oxidation
Card 1/3

Reactions of Fluoro Olefins. 13. Catalytic
Hydrogenation of Perfluoro Olefins

82692
S/062/60/000/008/006/012
B004/B054

hydrogenation of perfluoro butadiene yielded 1,1,2,3,4,4-hexafluoro butane which, with one mole of HF in 2,3-position splitting off, was transformed to $CF_2-CF=CH-CF_2H$. A table shows the boiling points of the compounds obtained. In the experimental part of the paper, the authors indicate the production of the Pd- and Ni catalyst, and the reactions performed, as well as the physical data and analyses of the compounds obtained. There are 1 table and 16 references: 3 Soviet, 5 US, 6 British, 1 Canadian, and 1 German. X

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk
SSSR (Institute of Elemental-organic Compounds of the
Academy of Sciences, USSR)

SUBMITTED: March 3, 1959

Card 3/3

S/062/60/000/008/031/033/XX
B013/B055AUTHORS: Konnyants, I. I. and Cheburkov, Yu. A.TITLE: Some α -Amino Acids Containing Trifluoromethylene GroupsPERIODICAL: *Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk*,
1960, No. 8, pp. 1516-1518

TEXT: This brief communication treats the addition of ethanol amine and diethanol amine to the ethyl ester of β, β -difluoromethyl acrylic acid. Under mild conditions, the reaction with ethanol amine gives N-(β -hydroxyethyl) hexafluoro valine ethyl ester. Only the amino- and not the OH group enters into reaction, though alcohols react equally readily with fluoroolefins, especially in alkaline medium. The structure of the product was confirmed by synthesizing it from the hexafluoro valine ester and ethylene oxide. The reaction can be carried out at room temperature in 50% acetic acid. With thionyl chloride, the N-(β -hydroxyethyl) hexafluoro valine ester is readily converted to the N-(β -chloroethyl) hexafluoro valine ester (II). The latter is transformed to the water-soluble N-(β -chloroethyl) hexafluoro valine (III) by hydrolysis with hydrochloric acid. Diethanol amine

Card 1/2

✓

Some α -Amino Acids Containing Trifluoromethylene S/062/60/000/008/031/033/XX
Groups B013/B055

did not react in the corresponding manner, even on heating to 150°C. The authors assume that the cause for the absence of an addition reaction between diethanol amine and β, β -bis(trifluoromethyl) methacrylate is to be sought in the steric hindrance due to the carbalkoxy groups, which prevent the di-(β -hydroxyethyl)-amino group from entering the α -position. At present, the biological activity of hexafluoro valine and its hydroxyethyl- and chloroethyl derivatives is being tested. There are 2 references: 1 Soviet and 1 US. ✓

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR (Institute of Elemental Organic Compounds of the Academy of Sciences USSR)

SUBMITTED: January 22, 1960

Card 2/2

87121

5.3700

1236.2209, 1262

S/062/60/000/009/017/021
B023/B064AUTHORS: Knudvants, I. I., Shokina, V. V., and Kuleshova, N. D.

TITLE: Addition of Hydrogen Halides to Fluoro Olefines

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh
nauk, 1960, No. 9, pp. 1693-1695

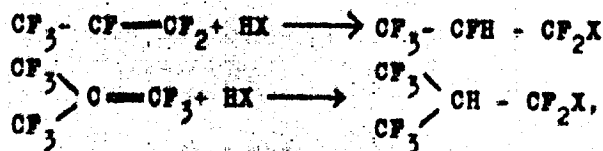
TEXT: The present investigation proved that it is easier to add hydrogen halides to perfluoro isobutylene than to perfluoro propylene. HF is, e.g., added to perfluoro isobutylene under pressure when heated to 200°. The reaction takes 24 h. Perfluoro propylene must be heated under the same conditions for 100 h at least. HCl and HBr are added in the vapor phase, without pressure, on a catalyst (coal in a mixture with CaSO_4). Addition to perfluoro isobutylene takes place at 200°C, while for perfluoro propylene the temperature must be raised to 230°C. The addition process corresponds to the distribution of the electron density in the olefine molecule. Thus, hydrogen is added to the carbon bound to the trifluoro methyl group:

Card 1/3

Addition of Hydrogen Halides to
Fluoro Olefines

87124

S/062/60/000/009/017/021
B023/B064



where X = F, Cl, Br. This is confirmed by comparing the spectra of the nuclear magnetic resonance of F^{19} in the compounds obtained with the spectra of compounds obviously containing the same groupings. The table p. 1694 shows the values of the relative chemical displacement for the compounds obtained. All attempts made to add perfluoro propylene to perfluoro isobutylene failed. The monohydro monohalogen perfluoro isobutanes were stable to acid and oxidizing reagents, e.g., to boiling with nitric acid (specific weight 1.52). Under the action of bases (NaHCO_3 , pyridine, aniline), hydrogen halide is readily split off again. Analogous propane derivatives are more stable. There are 1 table and 7 references: 1 Soviet, 4 US, and 3 British.

Card 2/3

LINIKOVA, M.G.; PASHINA, N.D.; KRYUKOVA, I.I.

Properties of α, α -diphenyl- β -propiothirolactone. Izv. AN SSSR Otd.
khim. nauk no.10:1825-1827 O '60. (MIRA 13:10)

1. Institut elementoorganicheskikh soedineniy Akademii nauk SSSR.
(Lactones)

06479

53630

1287, 2209, 1266

S/062/60/000/011/006/016
B013/B078

AUTHORS: Sterlin, R. N., Yatsenko, R. D., Pinkina, L. N.,
Kuvshinov, I. L.

TITLE: Perfluoro Derivatives of Nonmetals

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh
nauk, 1960, No. 11, pp. 1991 - 1997

TEXT: The preparation of perfluoro derivatives of phosphorus, arsenic, and antimony is described. From the reaction of perfluoro magnesium iodide with $AsCl_3$, PCl_3 , and $SbCl_3$ in ether solution only tertiary derivatives were obtained: tri-(trifluorovinyl)arsine, tri-(trifluorovinyl)phosphine, and tri-(trifluorovinyl)stibine. Primary and secondary derivatives were not formed in this process. Perfluorovinyl dichloroarsine was obtained by splitting 10-alkyl-5,10-dihydrophenarsazine with dry HCl (Ref.4). A corresponding perfluorovinyl derivative was obtained in a quantitative yield as a result of the reaction of perfluorovinyl magnesium iodide with adamsite. Perfluorovinyl chloroarsine was

Card 1/3

Perfluoro Derivatives of Nonmetals

86179

S/062/60/000/011/006/016
B013/B078

isolated in a practically quantitative yield by the reaction of $CF_2-CFAs(C_6H_4)_2NH$ with liquid HCl . By treating the tetraethyldiamide of phosphorous acid chloride and the tetraethyldiamide of ethyl phosphinic acid with dry, gaseous HCl in xylol solution, phosphorus trichloride, and ethyldichlorophosphine, respectively, were obtained. From the reaction of perfluorovinyl magnesium iodide with the tetraethyldiamide of phosphorous acid chloride, the tetraethyldiamide of perfluorovinyl phosphinic acid was obtained. This was converted into trifluorovinyl dichlorophosphine by reaction with dry HCl in ether solution. By treating the latter with antimony trifluoride, perfluorovinyl difluorophosphine was obtained. In a similar manner, the diethylamide of di-(trifluorovinyl) phosphinic acid was obtained from $(C_2H_5)_2NPCl_2$ and perfluorovinyl magnesium iodide. By decomposing it with dry HCl , di-(trifluorovinyl)chlorophosphine was synthesized. By treating the latter with antimony trifluoride, di-(trifluorovinyl)fluorophosphine was obtained. As opposed to the trifluoromethyl derivatives of arsenic and phosphorus, the prepared tri-(trifluorovinyl) arsine and tri-(trifluorovinyl)phosphine do not

Card 2/3

Perfluoro Derivatives of Nonmetals

06479

S/062/60/000/011/006/016
3013/B078

separate trifluoroethylene when heated. Thus, the perfluorovinyl radical in the said compounds does not show any properties of pseudohalogens. Ye. P. Shcherbina and L. F. Razgovorov assisted in this work. There are 8 references: 2 Soviet.

SUBMITTED: June 4, 1959

Card 3/3

86b01

15.8107

S/062/60/000/011/012/016
B013/B078

AUTHORS:

Dmitriyev, M. A., Artyev, P. T., Sokol'skiy, G. A.,
Knunyants, I. L.

TITLE:

Sulfurous Lactams and Their Polymers

PERIODICAL:

Investiya Akademii nauk SSSR. Otdeleniye khimicheskikh
nauk, 1960, No. 11, pp. 2053 - 2054

TEXT: In this brief paper an account is given of hitherto non-described polymers, which in the hydrocarbon chain contain sulfur atoms of sulfide and sulfon types. The lactam of β -aminoethoxy- α -propionic acid C_5H_9ONS , melting point $109^\circ-110^\circ C$ was produced by regrouping according to Beckmann by warming tetrahydro- γ -thiopyrroxime with concentrated sulfuric acid - yield 55%. It was possible to obtain the same lactam by reaction according to Schmidt by treating tetrahydro- γ -thiopyrroxime with hydrazoic acid - yield 50%. When in the latter case the excess of hydrazoic acid is used, this will yield in the reaction as the main product 1,2-tetrazole- β, β' -diethyl sulfide - $C_5H_8N_4S$, melting point $157^\circ C$. During oxidation of the

Card 1/2

Sulfurous Lactams and Their Polymers

86481
S/062/60/000/011/012/016
BC13/B078

lactam of β -amino ethoxy- α -propionic acid with hydrogen peroxide in glacial acetic acid, lactam of β -amino ethane sulfo- α -propionic acid - $C_5H_9O_3NS$ is formed - melting point $192^\circ-193^\circ C$ - yield 98%. Both lactams are colorless crystalline substances, soluble in water and in most organic solvents. When warming these lactams in the presence of various additions such as water, dry caustic lyes, or metallic sodium, a polymerization takes place under formation of respective polyamides:

$[-NH-CH_2-CH_2-S-CH_2-CH_2-CO-]_n$, $[-NH-CH_2-CH_2-SO_2-CH_2-CH_2-CO-]_n$. Polyamides are transparent fibers or foils insoluble in water and in most organic solvents. They are softened at temperatures of $\sim 200^\circ C$. There are 2 non-Soviet references.

SUBMITTED: April 18, 1960

Card 2/2

S/062/60/000/012/008/020
B013/B055

AUTHORS: Knunyants, I. L. and Cheburkov, Yu. A.

TITLE: Unsaturated Acids Containing Trifluoromethyl Groups. I.
Polarization of the Double Bond in β,β -Di(trifluoromethyl)
Acrylic Acid

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
1960, No. 12, pp. 2162-2167

TEXT: The addition of water, ammonia, and piperidine to β,β -di(trifluoromethyl)acrylic acid (I) and its ethyl ester (II) was realized in the present publication. In an acid medium and under extreme conditions (200°C, under pressure) the addition of water to the acid (I) yields β,β -di(trifluoromethyl) α -hydroxy propionic acid (III), which differs from the β -hydroxy acid described previously. Contrary to water, ammonia is added to the ester (II) under mild conditions at -80°C, forming the ethyl ester of hexafluoro valine (IV). Its structure was confirmed by saponification in acid medium followed by transformation of the hexafluoro valine (V) obtained to the α -hydroxy acid (III). Hexafluoro valine amide (VIII) was prepared from β,β -di(trifluoromethyl)acrylic acid chloride. While treatment of aniline and piperidine with

Card 1/3

Unsaturated Acids Containing Trifluoromethyl
Groups. I. Polarization of the Double Bond
in β,β -Di(trifluoromethyl)Acrylic Acid

S/062/60/000/012/008/020
B013/B055

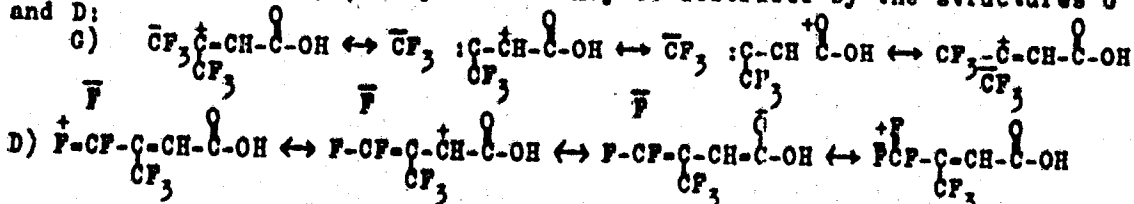
this acid chloride yields amides of the β,β -di(trifluoromethyl)acids (VI) and (VII), ammonia reacts also with the double bond. The structure of (VIII) was verified by transforming it to the α -hydroxy acid (III) by means of nitrous acid. Substitution reactions were not observed in the case of β,β -di(trifluoromethyl)acrylate. Both piperidine and ammonia add to the double bond, the former with formation of the ethyl ester of β,β -di(trifluoromethyl)- α -N-piperidyl propionic acid (IX). The structure of this compound was confirmed by its similarity to the addition products with ammonia and water and by the ready removal of all the fluorine atoms by alkaline hydrolysis. In the years 1953 to 1956, the addition of water, ammonia and hydrogen bromide to 7,7,7-trifluoro crotonic acid and its esters was investigated (Refs. 6, 7, 8). In the competitive effect of the two electron acceptor groups, trifluoromethyl and carboxyl, on the double bond, the carboxyl group was found to have the greater influence thus determining the direction of addition to trifluoro crotonic acid. In the case of β,β -di(trifluoromethyl) acrylic acid, the combined effect of the two trifluoromethyl groups was stronger than that of the carboxyl group, so that the direction of polarization of the double bond was found to be reversed. According to the two types of reaction mechanism of the trifluoromethyl groups, the electron shifts in

Card 2/3

Unsaturated Acids Containing Trifluoromethyl Groups. I. Polarisation of the Double Bond in β,β -Di(trifluoromethyl)Acrylic Acid

S/062/60/000/012/008/020
B013/B055

β,β -di(trifluoromethyl) acrylic acid may be described by the structures O and D:



No products indicative of allyl rearrangement were found among the reaction products formed by addition to β,β -di(trifluoromethyl) acrylic acid and its esters. This seems to imply that structure G, which takes into consideration the polar effect (-I) of the trifluoromethyl group, is the determinative one. The explanation given here is not the only acceptable one, since steric factors which might be of great importance, were entirely disregarded. There are 11 references: 3 Soviet, 6 US, and 2 British.

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR
(Institute of Elemental-organic Compounds of the Academy of Sciences USSR)

SUBMITTED: July 2, 1959
Card 3/3

S/062/60/000/012/009/020
B013/B055

AUTHORS:

Knunyants, I. L. and Cheburkov, Yu. A.

TITLE:

Unsaturated Acids Containing Trifluoromethyl Groups.
II. Free-radical Addition of Hydrogen Bromide to β,β -Di(tri-
fluoromethyl)Acrylic Acid

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
1960, No.12, pp. 2168-2172

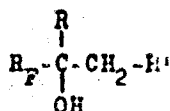
TEXT: The free-radical addition of hydrogen bromide to β,β -di(trifluoro-
methyl)acrylic acid was realized in the present work. Dry hydrogen bromide
adds to β,β -di(trifluoromethyl)acrylic acid (I) both under the conditions
of a free-radical reaction and without addition of an initiator (in presence
of an inhibitor), forming β,β -di(trifluoromethyl)nonobromo propionic acid
(II) in high yield. In order to establish the structure of (II), the authors
tried to substitute the hydroxyl group in the previously prepared (Ref. 3)
ethyl ester of α,α -dihydroperfluoro- β -hydroxy isovaleric acid (III) by bromine.
(III) reacted with phosphorus tribromide only under extreme conditions,
forming (II) but also β,β -di(trifluoromethyl)acrylic acid and its esters (IV)

Card 1/3

Unsaturated Acids Containing Trifluoromethyl
Groups. II. Free-radical Addition of
Hydrogen Bromide to β,β -Di(trifluoromethyl)
Acrylic Acid

9062/60/000/012/009/020
B013/B055

owing to the occurrence of dehydration under these reaction conditions. (III) -
reacts with thionyl chloride in presence of pyridine in a similar manner.
 α,α -dihydroperfluoro- β -hydroxy isovaleric acid reacts with an equimolar
amount of thionyl chloride under dehydration, forming β,β -di(trifluoro-
methyl)acrylic acid, whereas with 2 mole thionyl chloride or phosphorus
pentachloride it forms the acid chloride of β,β -di(trifluoromethyl)acrylic
acid (V) which is identical with the product obtained by treatment of (I)
with thionyl chloride. The splitting off of water from the hydroxy-acid
ester (III) under the action of thionyl chloride, which takes place under
comparatively mild conditions is a somewhat unusual reaction, since the
dehydration of compounds of the type



is known as difficult. Introduction of halogen into the β -position (re-
lative to the carboxyl) of β,β -di(trifluoro) β -propiolactone by means of
phosphorus pentachloride also gave β,β -ditrifluoromethyl acrylic acid

Card 2/3

Unsaturated Acids Containing Trifluoromethyl
Groups. II. Free-radical Addition of
Hydrogen Bromide to β,β -Di(trifluoromethyl)
Acrylic Acid

S/062/60/000/012/007/020
B013/B055

chloride. The structure of (II) was confirmed by hydrolytically splitting of the halogen at 135°C with water, whereby β,β -di(trifluoromethyl)- α -hydroxy propionic acid (VI) was obtained. The latter resembled the acid obtained in Ref. 1. The addition of hydrogen bromide to β,β -di(trifluoromethyl) acrylic acid proceeds by a radical mechanism. The reaction is catalyzed by peroxide and ultraviolet irradiation and inhibited by hydroquinone. Of the two possible intermediate radicals A and B formed during the attack on the double bond by the bromine radical, the free radical A is the more stable. This is in agreement with the data indicating that fluorinated tertiary radicals are more stable than secondary and tertiary radicals (Refs. 8, 9). There are 9 references: 3 Soviet, 4 US, and 2 British. ✓

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk
SSSR
(Institute of Elemental-organic Compounds of the Academy
of Sciences USSR)

SUBMITTED: July 2, 1959

Card 3/3

KNUNYANTS, I.L., akademik; VOROZHTSOV, N.N.

International Symposium in fluorine chemistry in Birmingham.
Zhur. VKHO 5 no.1:85-92 '60. (MIRA 14:4)

1. Chlen-korrespondent AN SSSR (for Vorozhtsov).
(Fluorine-Congresses)

KNUNYANTS, I.L.; CHEN' TSIN-YUN' [Ch'ŕn Ch'ing-yün]; GAMBARYAN, N.P.

Reaction of hexafluoroacetone with compounds containing active methylene groups. Zhur. VKHO 5 no.1:112-113 '60. (MIRA 14:4)

1. Institut elementoorganicheskikh soedineniy AN SSSR.
(Propanone) (Methylene group)

KNUNYANTS, I.L.; CHEN' TSIN-YUN [Ch'an Ch'ing-yün]; GAMBARYAN, N.P.;
ROKHILIN, Ye.M.

Reactions of hexafluoroacetone with phenols and aniline.
Zhur. VKHO 5 no.1:114-116 '60. (MIRA 14:4)

1. Institut elementoorganicheskikh soedineniy AN SSSR.
(Propanone) (Phenols) (Aniline)

5.3600
5.361080088
8/020/60/131/06/30/071
B011/2005

AUTHORS: Knunyants, I. L., Academician, Bykhovskaya, E. G.

TITLE: Interaction of Fluoroolefins With Hydrazoic Acid and Regrouping of Perfluoroalkenylasides

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 131, No. 6, pp. 1338 - 1341

TEXT: The authors discuss the statements made in Refs. 1-3. The first reaction scheme shows that 2 independent processes occur in the reactions of various compounds with perfluoroolefins: addition and substitution. Accordingly, the carbanion (I) formed as an intermediate is either stabilized to a saturated ether (II), or a vinylalkyl ether (III) is formed (Ref. 2). But the assumption that a four-membered transition complex (IV) is formed which is stabilized by the formation of an intramolecular hydrogen-H...F bond is also justified. This facilitates the elimination of HF and the formation of a product of vinyl substitution (see Scheme). Other experimental results of the addition of alcohols to φ -olefins agree with this interpretation (Ref. 3). The above rules are confirmed by the example of the hitherto not investigated reaction of φ -olefins with hydrazoic acid. φ -Propylene and φ -isobutylene with sodium-azide suspension

Card 1/3

80088

Interaction of Fluoroolefins With Hydrazoic Acid and Regrouping of Perfluoroalkenylazides S/020/60/131/06/30/071
B011/B005

in alcohol yield saturated β -monohydroperfluoropropyl- and β -monohydroperfluoroisobutylazide (see Scheme). The vinyl substitution occurs to a low extent in the case of ψ -isobutylene only. A product of vinyl substitution (V) in a noticeable yield was also obtained in the case of ψ -propylene by substitution of the solvent - polar alcohol - by nonpolar symmetrical tetrachloroethane in which the authors dissolved the triethyl-ammonium salt of hydrazoic acid. These products - perfluoroalkene azides - are very unstable, and automatically split off nitrogen at room temperature. The resulting "azacarbene" is subsequently regrouped (see Scheme). This may occur by transition of one nitrogen atom from the α -(VI), β -(VII), or γ -position (VIII), or by depairing of the electrons of the π -bond (IX). A colorless gaseous compound with the boiling point at -17° is formed by the reaction between ψ -propylene and HN_3 . On the basis of infrared spectrum analysis, the authors consider structures (VIII) and (IX) most probable. Structure (VIII) is, however, the most probable one. In contrast to all others, it has 4 non-equivalent positions of the fluorine atom. This is expressed by 4 signals in the spectrum of nuclear magnetic resonance (Fig. 1). The spectra were recorded by S. S. Dubov. Thus, the gas with the boiling point -17° is the perfluoroazacyclobutene-2 (VIII). Consequently, "perfluoropropenylazacarbene" is stabilized

Card 2/3

80088

Interaction of Fluoroolefins With Hydrazoic Acid and
Regrouping of Perfluoroalkenylazides

S/020/60/131/06/30/071
B011/B005

from the γ -position by transition of a fluorine atom to nitrogen. This process is similar to an ordinary allyl regrouping, and occurs in consequence of the conjugation of bonds in "azacarbene". In contrast to the very unstable perfluoroalkenylazides, β -monohydroperfluoroalkylazides are stable, easily distillable liquids which are not changed by heating with water and with 1/10 N alkalis. This confirms once more that the perfluoroalkenylazides are not formed by the separation of HF from saturated monohydroperfluoroalkylazides, but by substitution of a fluorine atom on the vinyl group in the φ -olefins. There are 1 figure and 4 references, 1 of which is Soviet.

SUBMITTED: January 30, 1960

Card 3/3

80058

S/020/60/132/01/32/064
B011/B1265.3600
AUTHORS:Knunyants, I. L., Academician, Bykhovskaya, E. G., Frosin, V. N.,
Kissel', Ya. M.

TITLE:

The Interaction of Fluorolefines With Nitrosyl Fluoride

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 132, No. 1, pp. 123-126

TEXT: The authors have shown that the reaction named in the title occurs easily: Nitrosyl fluoride (NOF) is added to the double bond $>C=C<$. Thus, on the reaction of nitrosyl fluorides with η -isobutylene, tert- η -nitrosoisobutane forms (boiling point $+24^{\circ}$). 2-Nitroso- η -propane (boiling point -13°) was prepared from η -propylene and NOF. η -ethylene certainly reacts with NOF, but η -nitrosoethane was not obtained. The latter reacts with the η -ethylene excess and gives perfluoro-2-ethyl-1,2-oxacetidine as the main product of the reaction (analogous to Ref. 5). On the other hand, surprisingly, η -nitrosoethane was obtained from the reaction of NOF with trifluoroethylenes. It is a blue gas with a boiling point of from -42° to -43° . Its formation is explained by means of chemical equations. The reaction of NOF and vinylidene fluorides is even more complicated: The single product obtained from it has the summation formula $(C_2F_3N_2OH)_x$. The

Card 1/3

00484

8/020/60/132/02/31/067

B011/B002

5.3600
5.3610

AUTHORS: Knunyants, I. L., Academician, Bykhovskaya, E. G., Frosin, V. N.

TITLE: Rearrangement of α,α -Difluoroalkylasides

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 132, No. 2, pp. 357-359

TEXT: By heating β -monohydroperfluoropropyl- and β -monohydroperfluoroisobutylasides up to 200°, the authors obtained corresponding carbylamine fluorides. The structure of the carbylamine fluorides obtained from the thermal rearrangement of α,α -difluoroalkylasides had to be determined. From the reaction of α -monohydroperfluoroisopropylcarbylamine fluoride with aniline, the authors obtained urea identical with that obtained from α -monohydroperfluoroisopropylisocyanate and aniline (Scheme). In order to obtain the isocyanate mentioned, the reaction between η -isobutylene and hydroxylamine (Ref. 2) was applied. The α -monohydroperfluoroisobutyrohydroxamic fluoride thus developing, was transformed into the acid chloride of the same acid on reaction with liquid HCl. Treated with silver benzoate, this acid chloride produced the benzoyl derivative of α -monohydroperfluoroisobutyrohydroxamic acid. On heating, this derivative rearranged itself and developed α -monohydroperfluoroisopropyliso-

Card 1/2

Rearrangement of α,α -Difluoroalkylazides

80484

S/020/60/132/02/31/067
B011/B002

cyanate (Scheme). The rearrangement of the perfluoroalkenazides via the corresponding "perfluoroalkenylazacarbene" was expected, as it seems, to develop a tricyclic nitrogen-containing compound. Such "azacarbene" however, as has been already published (Ref. 2), actually develop in such a way that one fluorine atom of the β -position passes over into the nitrogen. Due to the conjugation of bonds, such rearrangement probably takes place more quickly than a "depairing" of the electrons of the π bond whose electron density is exhausted (Scheme). By "azacarbene" the authors mean nitrogen-containing analogs of carbenes. They develop by the generally known rearrangement of acid azides (Curtius rearrangement) resulting in the development of isocyanates. Azacarbene is stabilized in the form of isocyanates. The above-mentioned reaction developing carbamate fluorides is similar to the Curtius rearrangement. There are 2 Soviet references.

SUBMITTED: January 30, 1960

Card 2/2

S/020/60/132/03/31/066
B011/B008

5.3610

AUTHORS: Knunyants, I. L., Academician, Sokol'skiy, G. A.

TITLE: A New Regrouping of the Trihalogenacetohydroxamic Acids

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 132, No. 3,
pp. 602-605

TEXT: Fluorine- and chlorine-substituted acetohydroxamic acids form easily by reaction of the esters of corresponding halogen-acetic acids with free hydroxylamine in an absolutely alcoholic solution. Monofluoro-, trichloro-, fluoro-, dichloro- and trifluoro-acetohydroxamic acids were produced in this way. They are colorless, hygroscopic crystalline substances, easily soluble in water, alcohols and acids, and partly soluble in most organic solvents. Aqueous solutions of the trifluoro-acetohydroxamic acid show different basicity, according to the duration of storage (Fig. 1). The authors presume in this connection the existence of a dynamic equilibrium of 2 tautomeric forms of this acid. 37% at least of the 2-basis form should be contained in a diluted aqueous

Card 1/3

A New Regrouping of the
Trihalogenacetylhydroxamic Acids

8/020/60/132/03/31/066
B011/B008

solution (see Scheme). Most of the hydroxamic acids together with their salts and the acyl derivatives tend to the regrouping by Lossen, with corresponding isocyanates or transformation products of the latter developing. The authors assumed that the regrouping of other halogen-substituted derivatives of the acetylhydroxamic acids can also proceed according to the general type of the reaction by Lossen with a possible subsequent transformation of the isocyanates. For the purpose of checking this assumption, the authors studied the thermal decomposition of the trichloro- and trifluoro-acetylhydroxamic acids. It became evident that an energetic decomposition occurs at the heating of these substances above their melting temperature. Surprisingly, the following substances develop here as the main reaction products: trichloro- and trifluoro-nitroso-methane and formaldehyde. At the same time, small quantities of HCN and CO₂ escape. The formation of nitroso compounds was not observed previously at the decomposition of hydroxamic acids. In consequence of a peculiar distribution of the electron density in the molecules of the completely halogenated hydroxamic acids and of the intermediates of their transformation, evidently a regrouping takes

Card 2/3

31231

**A New Regrouping of the
Trihalogenaceto-hydroxamic Acids**

S/020/60/132/03/31/066
B011/B008

place here, which deviates from the reaction by Lossen. The authors presume that the formation of a derivative "Asakarben" (Ref. 4) is the first stage of this regrouping. The formation of the "Asakarben" is apparently facilitated by the acidic-basic dissociation of the hydroxamic acids (see Scheme). The further stabilization of the "Asakarben" is achieved by the transition of the trihalogen-methyl-cation. A new nitrogen-carbon bond develops in consequence of the coordination of one of the undivided pairs of electrons of the nitrogen atom. The bipolar ion developing is hydrated. The sequence of the addition of the elements of the water appears to be opposed to the direction of reaction of the isocyanate hydration. The compound $X_3C-\overset{\text{OH}}{\underset{\text{H}}{\text{N}}}-\overset{\text{O}}{\text{C}}=O$ may be considered a

condensation product of the trihalogen-nitroso-methane with formaldehyde. It is decomposed thermally and forms the final products of the reaction (see Scheme). The above mentioned decomposition of the trihalogenaceto-hydroxamic acids is a new type of regrouping of the hydroxamic acids. There are 1 figure, 1 table, and 4 references, 1 of which is Soviet.

SUBMITTED: February 15, 1960

Card 3/3

KHONYANTS, I.L., Akademik; GOLUBEVA, N.Ye.; KIL'DISHEVA, O.Y.

Cancerolytic peptides of directional activity. Dokl.AN SSSR 132
no.4:836-838 Ja '60. (MIRA 13:5)
(Peptides)

CHEN 'TSIN-YUN'; GAMBATYAN, N.P.; KHUNYANTS, I.L., akad.

Bond conjugation in 1,1-bis(trifluoromethyl)-2-nitroethylene and
hexafluoroisopropylidenemalonate ester. Dokl.AN SSSR 133 no.5:
1113-1116 Ag '60. (MIRA 13:8)

1. Institut elementoorganicheskikh soedineniy Akademii nauk
SSSR.

(Chemical bonds) (Malonic acid) (Ethylene)

ROKHILIN, Ye.M.; GAMBARYAN, M.P.; CHEN' TSIN-YUN' [Ch'in Ch'ing-yün];
KNUNYANTS, I.L., akademik

2-Phenyl-4-hexafluoroisopropylidene-5-oxasolone. Dokl. AN SSSR 134
no.6:1367-1370 O '60. (MIRA 13:10)

1. Institut elementoorganicheskikh soedineniy Akademii nauk SSSR.
(Oxasolinone)

KNUNYANTS, I.L., akademik; KULESHOVA, M.D.; LIN'KOVA, M.G.

Structure of the products from the addition of alkyl sulfenyl
chlorides to unsaturated acids. Dokl. AN SSSR 135 no.1:81-83 N°60.
(MIRA 13:11)

1. Institut elementeorganicheskikh soedineniy AN SSSR.
(Sulfenyl chloride)

53600

86044

S/020/60/135/003/028/039
B016/B054

AUTHORS: Rokhlin, Ye. M., Gambaryan, N. P., and Knunyants, I. L.,
Academician

TITLE: Mobility of Fluorine Atoms in Derivatives of Benzamido
Hexafluoro Dimethyl Acrylic Acid - 7

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 135, No. 3,
pp. 613 - 616

TEXT: The authors report on their investigations of the saponification of fluorine atoms of the trifluoro methyl group in α -benzamido hexafluoro dimethyl acrylic acid (I) and its derivatives. They proved that fluorine atoms are very easily saponified. In the reaction with a saturated NaHCO_3 solution at room temperature, (I) is transformed into the salt of 1-benzamido-2-trifluoro-methyl-ethylene-1,2-dicarboxylic acid (II). The authors state that (III), the esters of acid (I), behave similarly; but 2-phenyl-4-carbalkoxy-5-trifluoro-methyl-1,3-oxazinones-6 (V) are also formed besides the acid esters (IV) of acid (II). In the authors' opinion, this is due to a cyclization of the intermediate acid fluorides (VI). By a Card 1/4

86044

Mobility of Fluorine Atoms in Derivatives of S/O20/60/135/003/028/039
Benzamido Hexafluoro Dimethyl Acrylic Acid B016/B054

reaction of acid esters (IV) with diazomethane, the authors obtained corresponding saturated esters: dimethyl ester (VII) and methyl-ethyl ester (VIII). (VII) is also formed in the methylation of the dicarboxylic acid (II) with diazomethane, whereas (VIII) is formed by a reaction of 2-phenyl-4-carbethoxy-5-trifluoro-methyl-1,3-oxazinone-6 with methanol in the presence of triethylamine. The saponification of the trifluoro methyl group in acid (I) and its derivatives proceeds easily, not only in alkaline medium. When boiling acid (I) with the hydrochloric acid solution of 2,4-dinitro-phenyl hydrazine, the authors isolated the 2,4-dinitro-phenyl hydrazone of α -trifluoro-methyl malonic semialdehyde (X). In the authors' opinion, this is due to a decarboxylation and saponification of one of the trifluoro methyl groups. The authors explain the very easy saponification of the trifluoro methyl group in acid (I) and its derivatives by the conjugation of the C-F bonds not only with the C=C double bond but also with the unseparated electron pair of the nitrogen atom. There are 4 references: 1 Soviet, 1 US, and 2 British.

Card 2/4

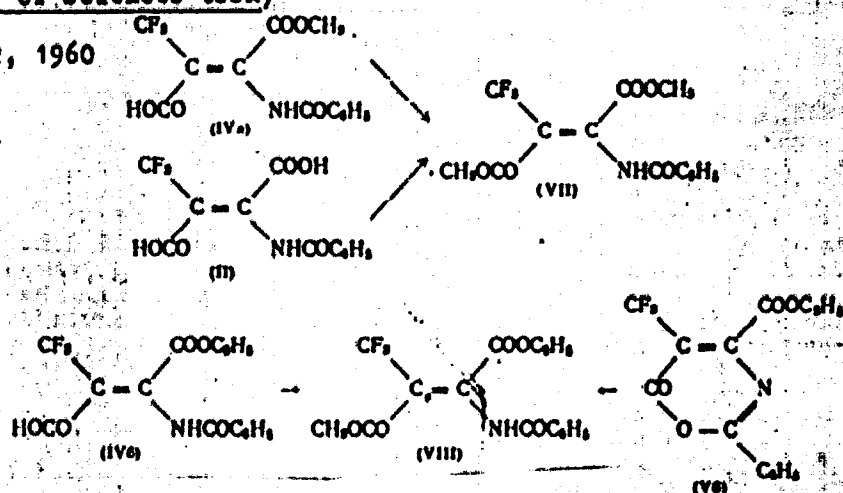
86044

Mobility of Fluorine Atoms in Derivatives of
Benzamido Hexafluoro Dimethyl Acrylic Acid

8/020/60/135/003/028/039
B016/B054

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk
SSSR (Institute of Elemental-organic Compounds of the
Academy of Sciences USSR)

SUBMITTED: July 12, 1960



Card 3/4

KATRENKO, Dmitriy Alekseyevich; SMIRNYAGINA, Aleksandra Andreyevna;
KNUNYANTS, I.L., akademik, nauchnyy red.; KORNILOVA, M.I.,
red.; BRIKIN, S.T., tekhn. red.

[Science outstrips fancy] Nauka, obgoniaishchaya mechtu. Mo-
skva, Izd-vo VsesPS Profizdat, 1961. 204 p. (MIRA 15:1)
(Synthetic products)

KNUNYANTS, I.L., glav. red.; BAKHAROVSKIY, G.Ya., zam. glav. red.;
 HUSEV, A.I., red.; VARSHAVSKIY, Ya.M., red.; GEL'PERIN,
 N.I., red.; DOLIN, P.I., red.; KIREYEV, V.A., red.; MEYERSON,
 G.A., red.; MURIN, A.N., red.; POODIN, S.A., red.; REBINDER,
 P.A., red.; SLOVIMSKIY, O.S., red.; STEPANENKO, B.N., red.;
 EPSHTEYN, D.A., red.; VASKEVICH, D.N., nauchnyy red.; GALLE,
 R.R., nauchnyy red.; GARKOVENKO, R.V., nauchnyy red.; GODIN,
 Z.I., nauchnyy red.; MOSTOVENKO, N.P., nauchnyy red.;
 LEHEDEVA, V.A., mladshiy red.; TRUKHANOVA, M.Ye., mladshiy
 red.; FILIPPOVA, K.V., mladshiy red.; ZHAROVA, Ye.I., red.;
 KULIDZHANOVA, I.D., tekhn. red.

[Concise chemical encyclopedia] Kratkaya khimicheskaya entsiklo-
 pedia. Red. koll.: I.L.Knuniants i dr. Moskva, Gos. nauchn.
 izd-vo "Sovetskaya entsiklopediya." Vol.1. A - Z. 1961.
 1262 columns. (MIRA 15:2)

(Chemistry—Dictionaries)

KHUMYANTS, I.L.; RYTSLIN, E.Ye.; GARDIANYAN, N.P.

β -Lactams. Report No. 4: Synthesis of 3,3-diphenyl-2-azetidinones.
Izv. AN SSSR, Otd. khim. nauk no. 1:83-88 Ja '61. (MIRA 14:2)

1. Institut elementoorganicheskikh sovedineniy AN SSSR.
(Azetidinone)

KNUNYANTS, I.L.; PERVOVA, Ye.Ya.; TYULENEVA, V.V.

Addition reactions of perfluoroolefins. Report No. 14: Conjugated
addition of halides and mercury salts. Izv. AN SSSR. Otd. khim.
nauk no. 1:88-93 Ja '61. (MIRA 14:2)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.
(Olefins) (Mercury organic compounds)
(Fluorine organic compounds)

SOKOL'SKIY, G.A.; DMITRIYEV, M.A.; KNUNYANTS, I.I.

Fluorinated β -sultones. Report No. 5: Reaction of tetrafluoroethane-
 β -pyrosultone with alcohols. Izv.AN SSSR Otd.khim.nauk no.4:617-620
Ap '61. (MIRA 14:4)

(Sultone)

SOKOL'SKIY, G.A.; DMITRIYEV, M.A.; KNUNYANTS, I.L.

Fluorinated β -sultones. Report No. 6: Sulfonyl fluoride mono-
fluoroacetic acid. Inv.AN SSSR Otd.khim.nauk no.4:621-622 Ap '61.
(MIRA 14:4)

(Acetic acid) (Sultone)

KHUNYANTS, I.L.; CHEBURKOV, Ya.A.

Fluorine-containing β -lactones. Report No.2: β -trifluoromethyl-
 β -methyl- β -propiolactone. Izv.AN SSSR.Otd.khim.nauk no.5:808-
810 My '61. (MIRA 14:5)

1. Institut elementoorganicheskikh soedineniy AN SSSR.
(Hydracrylic acid)

KNUNYANTS, I.L.; CHEBURKOV, Yu.A.

Fluorine-containing β -lactones. Report No. 3: Reactions of opening of
four-membered ring of β -trifluoromethyl- β -methyl- β -propiolactone.
Izv. AN SSSR. Otd. khim. nauk no. 5: 811-813 My '61. (MIRA 14:5)

1. Institut elementoorganicheskikh soedineniy AN SSSR.
(Hydroacrylic acid)

SOKOL'SKIY, G.A.; KNUNYANTS, I.L.

Fluorine-containing β -sulfones. Report No.7: Use of tetra-
fluoroethane- β -sulfone in the acetylation reaction. Izv. AN SSSR.
Otd.khim.nauk no.5:813-815 My '61. (MIRA 14:5)
(Sulfone) (Acetylation)

SOKOL'SKIY, G.A.; KNUNYANTS, I.L.

Fluorine-containing β -sultones. Report 8: β -Sultones, promoters
of acylation. Izv. AN SSSR, Otd. khim. nauk no. 6, 1053-1055, Je '61.
(MIRA 14:6)

(Sultones) (Acylation)

SOKOL'SKIY, G.A.; DMITRIYEV, M.A.; KNUNYANTS, I.L.

Fluorine-containing β -sultones. Report 9: Reactions between
fluorine-containing β -sultones and mercaptans. Izv. AN SSSR.
Otd.khim.nauk no.6:1055-1057 Je '61. (MIRA 14:6)
(Sultones) (Thiols)

KHUNYANTS, I.L.; CHEBURKOV, Yu.A.

Unsaturated acids containing trifluoromethyl groups. Report 3:
Polarisation of the double bond in β -trifluoromethylcrotonic
acid. Izv. AN SSSR, Otd. khim. nauk no. 6: 1057-1062 Je '61. (MIRA 14:6)

1. Institut elementoorganicheskikh soedineniy AN SSSR.
(Crotonic acid)

KARPAVICHUS, K.I.; GOLUBEVA, M.Ye.; KIL'DISHEVA, O.V.; KNUNYANTS, I.L.

Cancerolytic peptides having specific action. Report No.2:
p-Di-(chloroethyl)amino-D,L-phenylalanyl-D,L-valine. Isv.
AN SSSR. Otd.khim.nauk no.7:1297-1299 J1 '61. (MIRA 14:7)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.
(Valine)

KARPAVICHUS, K.I.; GOLUBEVA, N.Ye.; KIL'DISHEVA, O.V.; KNUNYANTS, I.L.

Cancerolytic peptides having specific action. Report No.3:
N-[p-di(2-chloroethyl)-aminophenacetyl] and N-(p-di(2-chloroethyl)-aminophenylbutyl) amino acids. Izv. AN SSSR. Otd.khim.nauk
no.7:1299-1303 J1 '61. (MIRA 14:7)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.
(Amino acids)

158160

2209

26403
S/062/61/000/008/007/010
B117/B206

AUTHORS:

Knunyants, I. L., Li Tjih-ydan, and Shokina, V. V.

TITLE:

α,ω -perfluoro diolefins and some of their conversions

PERIODICAL:

Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 8, 1961, 1462-1468

TEXT: During telomerisation of tetrafluoro ethylene with 1,2-dichloro iodine perfluoro ethane by application of benzoyl peroxide as initiator, the authors succeeded in producing lowest telomer homologues and highest telomers with good yield: $CF_2Cl \cdot CFCI \cdot nCF_2=CF_2 \rightarrow CF_2ClFCI(CF_2CF_2)_nI$ with $n=1, 2, 3, 4$ (Tables 1 and 2). They are waxy substances. The ratio of telomers in reaction products depends, as always, on the reaction conditions and the amount of Telogen used. In all experiments, benzoyl peroxide amounted to 1 % of the weight of dichloro iodine perfluoro ethane used. Through the effect of metallic zinc on the telomeric solutions in methylene chloride, $\alpha,\beta,\gamma,\omega$ -tetrachloro perfluoro alkanes (Table 3) were obtained in the presence of acetic anhydride. They were converted into

Card 1/1

26403

S/062/61/000/008/007/010

B117/B206

α,ω -perfluoro diolefins and some...

α,β -perfluoro dienes (Table 4) by dechlorination with zinc in acetic acid. Perfluoro octadiene-1,7, perfluoro dodecadiene-1,11 and perfluoro hexadecadiene-1,15 were produced in this way. Moreover, by doubling the mixtures of various telomers, tetrachlorides were produced. Through their rectification, 1,2,5,6-tetrachloro perfluoro hexane and 1,2,9,10-tetrachloro perfluoro decane were isolated. By dechlorinating 1,2,9,10-tetrachloro perfluoro decane, perfluoro decadiene-1,9 was obtained. By oxidation with potassium permanganate, all the α,ω -perfluoro diolefins in aqueous acetone solution were converted into corresponding perfluorated dicarboxylic acids with good yield: $\text{HOOC}(\text{CF}_2\text{CF}_2)_n\text{COOH}$, $n=2, 3, 4$ and 6

(Table 5). From perfluoro adipic- and perfluoro sebacic acid, chlorides of these acids were produced for the first time under the effect of thionyl chloride in the presence of catalytic amounts of KCl or KOH. From these chlorides, dianilide and diamide were produced. During the polycondensation of perfluoro adipic- and perfluoro sebacic acid chlorides with hexamethyl diamine, fluorated polyamides were produced between two media (water- CCl_4). There are 7 tables and 7 references: 1 Soviet and 6 non-Soviet. The three most recent references to English-

Card 2/6

72101

α,ω-perfluoro diolefins and some...

3/062/61/000/008/007/010
B117/B206

language publications read as follows: M. Hauptschein, M. Braid,
F. E. Lawlor, J. Amer. Chem. Soc. 79, 2549 (1957); A. L. Henne,
Wm. Postelneck, J. Amer. Chem. Soc. 77, 2334 (1955); R. A. Guenther,
pat. USA 2606206 (1952).

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk
SSSR (Institute of Elemental-organic Compounds, AS USSR)

SUBMITTED: August 1, 1960

Table 1: Reaction conditions and yield of telomer homologs. Legend:
1) Ratio $CF_2ClCFClI$ to $CF_2=CF_2$; 2) reaction temperature, °C; 3) duration of
reaction, hr; 4) yield of telomers, %; 5) calculated per reacting 1,2-di
chloro iodine
perfluoro ethane.

Oxidation ratio ①	Temperature ②	Reaction time ③	④ Yield telomers, %		
			n=1	n=2	n=3
2:1	135	4	62.4	19.8	—
1:1	150	5	37.0	24.0	4.5
1:2	150	4	38.2	23.0	25

Card 3/6

SONOL'SKIY, G.A.; KUMYANTS, I.L.

Fluorine-containing β -sulfones. Report No.10: Refraction
values of a sulfonyl fluoride group. Izv. AN SSSR. Otd.khim.
nauk no.8:1468-1471 Ag '61. (MIRA 14:8)
(Sulfonyl fluoride)
(Refraction)

KNUNYANTS, I.L.; CHEBUREKOV, Yu.A.; MAKAROV, Yu.V.

Thermal decomposition of alcoholates of tertiary alcohols
containing trifluoromethyl groups. Izv. AN SSSR. Otd.khim.
nauk no.8:1471-1475 Ag '61. (MIRA 14:8)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.
(Alcohols) (Alcoholates)

KAUNYANTS, I.L.; GERMAN, L.S.; DYATKIN, B.L.

α -Bromoperfluoroisobutyric acid and its derivatives. Izv.
AN SSSR. Otd.khim.nauk no.8:1513-1514 Ag. '61. (MIRA 14:8)

1. Institut elementoorganicheskikh soedineniy AN SSSR.
(Isobutyric acid)

SOKOL'SKIY, G.A.; KNUNYANTS, I.L.

Fluorine-containing β -sultones. Report No.11: Preparation of
fluoromethane and difluoromethanesulfonyl fluorides. Izv. AN SSSR.
Otd.khim.nauk no.9:1606-1610 9 '61. (MIRA 14:9)
(Methane) (Methanesulfonyl fluoride)

KNUNYANTS, I.L.; LI CHZHI-YUAN* [Li Chih-yüan]

Fluorinated monocarboxylic acids. Izv. AN SSSR. Otd. khim. nauk
no. 10: 1910-1911 O '61. (MIRA 14:10)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.
(Acids, Organic) (Fluorine compounds)

STERLIN, R.N.; LI VEY-GAN; KNUNYANTS, I.L.

Reactions of perfluorodivinymercury. Zhur.VKHO 6 no.1:106-109
'61. (MIRA 14:3)

(Mercury)

STERLIN, R.M.; DUBOV, S.S.; LI VEY-QAN; VAKHONCHIK, L.P.; KHUNYANTS, I.L.

Certain regularities in the series of perfluorovinyl derivatives
of the elements of groups IV and V of the periodic table.

Zhur.VKHO 6 no.1;110-111 '61.
(Vinyl compounds)

(MIRA 14:3)

KNUNYANTS, I.L.; GERMAN, L.S.; DYATKIN, B.L.; MOCHALINA, Ye.P.

Condensation of 1,2-difluoro-1,2-dichloroethylene with formaldehyde.
Zhur.VKHO 6 no.1:114 '61. (MIRA 14:3)

1. Institut elementoorganicheskikh soedineniy Akademii nauk SSSR.
(Ethylene) (Formaldehyde)

KNUTSAND, I.L., akademik

Origin and treatment of cancer. Nauka i zhizn' 28 no.7:18-21
Jl '61.

(MIRA 14:8)

(CANCER RESEARCH)

KNUNYANTS, I.L., akademik; LI CHEHI-YUAN' [Li Chih-yuan]; SHOKINA, V.V.

Mechanism of the addition of iodine chloride to chlorotrifluoroethylene.
Dokl. AN SSSR 136 no. 3:610-612 Ja '61. (MIRA 14:2)

1. Institut elementoorganicheskikh soedineniy AN SSSR.
(Iodine chloride) (Ethylene)

KNUNYANTS, I.L., -akademik; CHEBURKOV, Ya.A.

Manifestation of pseudohalogen properties by a trifluoromethyl
group bound to a carbon atom. Dokl.AN SSSR 137 no.5:1121-1124
Ap '61. (MIRA 14:4)
(Trifluoromethyl group)

FOKIN, A.V., SKLADNEV, A.A., KHUMYANTS, I.L., akademik

Reactions of fluorinated olefins. Reactions between fluorinated
olefins and hydrogen sulfide. Dokl. AN SSSR 138 no.5, 1132-1135, 1961. (MIRA 14:6)

(Olefins)

(Hydrogen sulfide)

15.8160

25481
8/020/61/139/001/013/018
B103/B226

AUTHORS:

Dyatkin, B. L., Mochalina, Ye. P., and Knunyants, I. L.,
Academician

TITLE:

Condensation of formaldehyde with perfluoro olefines -
tetrafluoro ethylene, hexafluoro propylene, and trifluoro
chloroethylene

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 139, no. 1, 1961, 106-109

TEXT: The authors continued the investigation of chlorosulfonic acid as a catalyst of H. Prins' reaction (Ref. 1: Rec. trav. chim., 51, 469 (1932)) and endeavored to use this acid when extending the Prins reaction to perfluoro olefines: tetrafluoro ethylene, hexafluoro propylene, and trifluoro chloroethylene, in their interaction with formaldehyde. As is known, the Prins reaction belongs to the typical reactions of hydrocarbon olefines with electrophile reagents; especially, in this case, the condensation with formaldehyde in the presence of strong acids is meant. Such reactions are very difficult and, therefore, little investigated. The authors demonstrated by means of 1,2-difluoro-1,2-dichloro ethylene that

Card 1/5

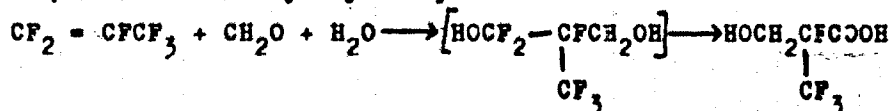
25481

S/020/61/139/001/013/018

B103/B226

Condensation of formaldehyde...

both chlorosulfonic and fluorosulfonic acid are in this case highly effective catalysts of the Prins reaction, while H_2SO_4 of various concentrations could not release this reaction (I. L. Knunyants et al. Ref. 5: Zhurn. Vsesoyuzn. khim. obshch. im. Mendeleyeva, 6, 114 (1961)). It has been proved that a mixture of tetrafluoro ethylene $CF_2 = CFCF_3$, paraformaldehyde, and chlorosulfonic acid, heated up to $100^\circ C$, is subject to a condensation according to the general scheme of the Prins reaction, and yields α, α -difluoro hydracrylic acid which is isolated as its ethyl ester. As the yield of this ester was 62.6 %, the authors were of the opinion that chlorosulfonic acid is much more active than H_2SO_4 . The condensation of paraformaldehyde with hexafluoro propylene leads in the presence of chlorosulfonic acid at $130 - 150^\circ C$ to a 41-% yield of α -fluoro- α -trifluoro methyl hydracrylic acid:



Card 2/5